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Structure of Trirubidium Hydrogenbis(sulfate), $Rb_3H(SO_4)_2$

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Abstract. $M_r = 449{\cdot}5$, monoclinic, $C2/c$, $a = 15{\cdot}144\ (3)$, $b = 5{\cdot}890\ (3)$, $c = 10{\cdot}149\ (1)$ Å, $\beta = 102{\cdot}55\ (1)°$, $V = 883{\cdot}7$ Å^3, $Z = 4$, $D_x = 3{\cdot}380$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 16{\cdot}58$ mm^{-1}, $F(000) = 832$, $T = 292$ K, final $R = 0{\cdot}048$ for 1006 observed reflections. Trirubidium hydrogenbis(sulfate) is isostructural with its triammonium analogue. The room-temperature structure for these two salts is pseudohexagonal and phase transitions to hexagonal symmetry at elevated temperatures are predicted to involve changes in the O—H—O hydrogen bonds.

Introduction. Since the discovery that triammonium hydrogenbis(sulfate) $[(NH_4)_3H(SO_4)_2]$ exhibits polymorphism and ferroelectric or antiferroelectric properties, dielectric measurements and differential thermal analyses have been carried out on $M_3H(SO_4)_2$-type compounds and their deuterated derivatives to gain an understanding of the successive phase transitions and ferroelectric properties of this class of compounds (Gesi, 1976, 1980; Ichikawa, 1978). The unit-cell parameters, space-group symmetry and morphology suggest the K and Rb analogues to be isostructural with the triammonium salt (Parry & Glasser, 1960; Suzuki & Makita, 1978)* and it was suggested that they would mimic the ferroelectric transitions of the latter. It has been found that whereas the ammonium salt undergoes three phase transitions between room and liquid-helium temperature, no indications of such transitions are detected for the Rb and K analogues (Gesi, 1976, 1980; Ichikawa, 1978). On heating, the triammonium salt undergoes a phase transition at 413 K (Gossner, 1904) whereas its trirubidium analogue undergoes successive phase transitions at 329 and 399 K (Ichikawa, 1978). To explain the phase transitions of triammonium hydrogenbis(sulfate), Suzuki & Makita (1978) proposed that the H atoms involved in O—H—O hydrogen bonds are in motion either statistically or dynamically between shallow double potential minima, but possible structural transformations of the ammonium ions were not ruled out.

Experimental. The salt was precipitated from sulfuric acid solutions of Rb_2SO_4 (Alpha Products, 99·9%) by addition of ethanol, and by mulling stoichiometric quantities of Rb_2SO_4 and H_2SO_4. Crystals were grown from aqueous solution by slow evaporation. The products were analyzed gravimetrically for sulfate-ion content, and by acid/base titration for hydrogen content.

Single-crystal data: colorless crystal, specimen approximately spherical, radius 0·078 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; cell parameters from least-squares refinement of 25 reflections with $12 \le \theta \le 24°$; 1932 unique reflections; 1006 considered observed at the $3\sigma(I)$ level; $\theta \le 35°$, θ–2θ scans; 3 standard reflections monitored after every 7200 s of exposure, max. variation in intensity −4·5%; Lp correction; spherical absorption correction, min., max. and ave. transmission factors 0·165, 0·198 and 0·183. Precession photographs showed the space group to be either Cc or $C2/c$; the latter was selected on the basis of the intensity statistics. Atomic coordinates of $(NH_4)_3H(SO_4)_2$ used as input for refinement. Full-matrix least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$, where $w = 4F^2/[\sigma^2(F^2) + (0{\cdot}06F^2)^2]$ with anisotropic temperature factors. The scattering factors used were those of Cromer & Waber (1974); the anomalous-dispersion coefficients were taken from Cromer (1974). Correction for isotropic secondary-extinction effect included in the refinement, $g = 0{\cdot}440 \times 10^{-5}$. Final $R = 0{\cdot}048$, $wR = 0{\cdot}057$, $S = 1{\cdot}339$ for all observed reflections; max. final $\Delta/\sigma = 0{\cdot}03$; max. and min. final $\Delta\rho$ excursions 0·945 and −1·084 e Å^{-3} found in the vicinities of the Rb atoms. Calculations on a PDP 11/23 computer using the *Structure Determination Package* of Enraf–Nonius (1979) and *ORTEP* by Johnson (1965).

Powder data: Powder diffraction patterns were recorded on a CSS/STOE STADI 2/PL diffractometer in transmission mode, with and without As_2O_3 as an

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* In a recent paper, Davis & Johnson (1984) assign a triclinic cell to $(NH_4)_3H(SO_4)_2$. This is a primitive subcell of the A-centered monoclinic cell chosen by Suzuki & Makita (1978) identified by the transformation matrix $(0,1,0;\ 1,0,0;\ 0,-\frac{1}{2},\frac{1}{2})$. We have examined our single-crystal data for the Rb salt, and find good intensity agreement for the measured ($hk0$ and $\bar{h}k0$) Laue class $2/m$ symmetry-related reflections. The value of $R_{\rm int}$ is 0·035, where $R_{\rm int} = \sum_i\sum_j|\bar{I}_i - I_{ij}|/\sum\bar{I}_i$. Our powder data on the ammonium salt are refined on the monoclinic cell to $F_{30} = 24(0{\cdot}0128,\ 97)$. We believe the monoclinic setting is to be preferred.

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internal standard. The cell parameters from the powder data refinement are $a = 15{\cdot}155\ (3)$, $b = 5{\cdot}892\ (1)$, $c = 10{\cdot}163\ (4)$ Å, $\beta = 102{\cdot}57\ (2)°$, with $F_{30} = 22\ (0{\cdot}0138, 96)$.* The powder data have been submitted to the Joint Committee on Powder Diffraction Standards (JCPDS file No. 35-1012).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$B_{\rm eq}$(Å^2)
Rb(1)	0·000	0·2585 (2)	0·750	1·63 (1)
Rb(2)	0·19239 (5)	0·7270 (1)	0·65238 (6)	1·79 (1)
S	0·1158 (1)	0·2201 (3)	0·4645 (1)	1·28 (2)
O(1)	0·1524 (3)	0·0268 (8)	0·4029 (4)	1·68 (8)
O(2)	0·0135 (3)	0·1799 (9)	0·4435 (5)	1·96 (9)
O(3)	0·1516 (3)	0·2312 (8)	0·6095 (4)	1·66 (8)
O(4)	0·1270 (3)	0·4320 (8)	0·3969 (4)	1·88 (9)

Table 2. *Bond distances* (Å) *and bond angles* (°)

Rubidium coordination			
Rb(1)–O(1)	3·000 (4)	Rb(1)–O(2)	3·195 (4)
Rb(1)–O(2)	3·223 (4)	Rb(1)–O(2)	3·830 (4)
Rb(1)–O(3)	2·958 (4)	Rb(1)–O(4)	2·829 (4)
Rb(2)–O(1)	2·940 (4)	Rb(2)–O(1)	3·038 (4)
Rb(2)–O(1)	3·099 (4)	Rb(2)–O(2)	3·107 (4)
Rb(2)–O(3)	2·990 (4)	Rb(2)–O(3)	2·997 (4)
Rb(2)–O(3)	3·045 (4)	Rb(2)–O(4)	3·013 (4)
Rb(2)–O(4)	3·100 (4)	Rb(2)–O(4)	3·515 (4)
Sulfate group			
S–O(1)	1·465 (4)	S–O(2)	1·535 (4)
S–O(3)	1·455 (4)	S–O(4)	1·452 (4)
O(1)–S–O(2)	106·5 (2)	O(1)–S–O(3)	112·0 (2)
O(1)–S–O(4)	111·9 (2)	O(2)–S–O(3)	106·9 (2)
O(2)–S–O(4)	106·6 (3)	O(3)–S–O(4)	112·6 (2)

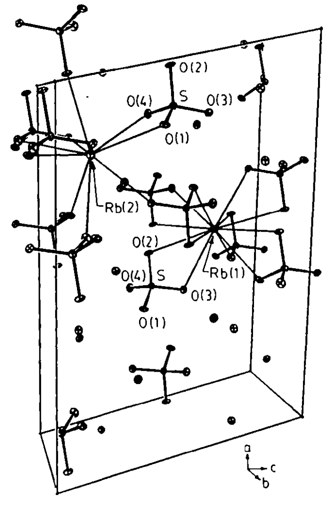

Fig. 1. A packing diagram of the unit cell.

Discussion. The atomic parameters and temperature factors are given in Table 1.* Interatomic distances for the coordination about the Rb atoms and bond lengths and angles for the sulfate group are given in Table 2. The crystal structure is shown in Fig. 1.

No major structural differences are found between trirubidium hydrogenbis(sulfate) and its ammonium analogue. The Rb^+ ions occupy two sets of non-equivalent positions. The Rb(1) coordination consists of ten O atoms from 2·829 (4) and 3·223 (4) Å; two additional O atoms are 3·830 (4) Å from the Rb. The Rb(2) ions are coordinated by nine O atoms from 2·940 (4) to 3·100 (4) Å; an additional O is at 3·515 (4) Å. The sulfate ion forms a distorted tetrahedron, with S—O(2) being significantly longer than the remaining three S—O bonds – a feature also observed in the triammonium hydrogenbis(sulfate) structure. In the latter structure, the O(2) atoms take part in O(2)—H—O(2′) hydrogen bonds, which link neighbouring SO_4^{2-} ions in pairs. In the present structure, the H atom could not be located unambiguously in the difference Fourier map. However, diffuse electron density of the order of 0·15 e Å^{-3} is found at 0,0,0, the coordinates of the corresponding H in the ammonium analogue structure. In view of the elongation of the S—O(2) bond and the fact that the H is either disordered or on a special position (since there is a total of only four H atoms in the unit cell) disordered and/or apparently symmetrical O(2)—H—O(2′) bonds are expected, as in the triammonium analogue structure. The O(2)···O(2′) distance is short, 2·485 (9) Å, in the present structure, as compared to 2·540 (2) Å in the ammonium analogue.

The triammonium salt becomes uniaxial above 413 K (Gossner, 1904). The high-temperature phase is presumably hexagonal and the trirubidium salt may undergo a similar phase transition at higher temperatures. A pseudo $R\bar{3}m$ unit cell with parameters $a = b = 5{\cdot}867$, $c = 22{\cdot}175$ Å, $\alpha = 89{\cdot}69$, $\beta = 90{\cdot}31$ and $\gamma = 119{\cdot}74°$ can be obtained by applying one of the transformations T_i, $i = 1, \ldots, 6$, where

$$T_i = R_{3i}\begin{pmatrix} 0 & \frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{3}{2} & 0 & \frac{1}{2} \end{pmatrix}$$

with R_{3i} = rotation matrices of point group $\bar{3}$. To obtain the atomic coordinates in the pseudohexagonal cell, the coordinates of the $C2/c$ cell are first shifted so that the twofold axes coincide in monoclinic and hexagonal cells. The usual transformation, $(T_i^{-1})_t$, applied to the shifted coordinates then gives the pseudohexagonal coordinates (Table 3). As expected, the largest

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* For a definition of the figure of merit F_{30} see Smith & Snyder (1979).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42120 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of pseudo and idealized hexagonal coordinates*

	Pseudohexagonal coordinates x,y,z	Idealized coordinates x,y,z	Difference (Å)
Rb(1)	0·0085, 0·0085, 0·0000	0·0000, 0·0000, 0·0000 0, 0, 0	0·050
Rb(2)	0·9721, 0·9819, 0·7949	0·0000, 0·0000, 0·7949 0, 0, z	0·199
O(1)	0·8413, 0·7121, 0·4349	0·8616, 0·7236, 0·4291 x, $2x$, z	0·166
O(3)	0·8388, 0·1235, 0·4344	0·8618, 0·1382, 0·4291 x, $-x$, z	0·166
O(4)	0·2441, 0·1198, 0·4180	0·2764, 0·1382, 0·4291 $-2x$, $-x$, z	0·296
O(2)	0·9075, 0·9521, 0·3423	0·0000, 0·0000, 0·3423 0, 0, z	0·470

deviation from hexagonal symmetry is for O(2), for which idealized coordinates correspond to those of a $3m$ special position. The pseudohexagonal structure is isotypic with $Ba_3(PO_4)_2$ (Zachariasen, 1948), a common structural type for trimetal sulfates, phosphates and chromates.

The observed structural features suggest that changes in the hydrogen bonds are present in the mechanisms of phase transitions above room temperature. They also suggest that the ammonium ions are involved in the phase transitions below room temperature, as they only occur for the triammonium salt.

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Structure of Silyl Fluoride, SiH_3F, at 96 K

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Abstract. $M_r = 50·08$, monoclinic, $P2_1/n$, $a = 7·7723$ (12), $b = 7·76731$ (21), $c = 4·6926$ (4) Å, $\beta = 96·491$ (5)°, $V = 281·48$ (9) Å^3, $Z = 4$, $D_x = 1·182$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·462$ mm^{-1}, $F(000) = 104$, $T = 96$ K, $R = 0·0572$ for 707 observed reflections. The structure comprises chains of molecules formed by intermolecular F···Si interactions. Perhaps surprisingly, there are no close F···H contacts. Concomitant with the 4 + 1 coordination at Si in the crystal a lengthening of the Si—F bond to 1·6045 (14) Å is observed, relative to the gas-phase value of 1·59465 (4) Å.

Introduction. As part of our continuing work in this department on the structures of low-melting inorganic compounds, we are interested in species whose vibrational spectra change significantly with phase, for example $N(CH_3)_2SiH_3$ (Blake, Ebsworth & Welch, 1984), SiH_3OSiH_3 (Barrow, Ebsworth & Harding, 1979) and SiH_3CN (Barrow, 1985). Here we report the crystal structure of silyl fluoride, in which the frequency of ν(Si—F) decreases sharply between the vapour (872 cm^{-1}) and solid (804 cm^{-1}).

Experimental. Colourless, cylindrical crystal, 0·04 × 0·04 × 0·03 cm, grown *in situ* on low-temperature-equipped Weissenberg goniometer from sample sealed in Pyrex capillary, space group identified by oscillation and Weissenberg photography. D_m and m.p. not determined – compound lacks well defined liquid phase at ambient pressure. Crystal transferred without melting as described previously (Blake, Cradock, Ebsworth,

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